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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the Transport of Dangerous Goods
(Fourteenth session,
Geneva, 8-18 December 1997,
agenda item 2(d))

DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Other draft amendments

Copper sulphate and copper sulphate solution

Transmitted by the Expert from Germany

1. Large volumes of copper sulphate and copper sulphate pentahydrate are shipped. Copper solutions are of industrial importance not only used as a basis for fungicidal or algicidal preparations. Copper solutions are dangerous to human health and water organisms. Concentrated solutions of copper sulphate are damaging metallic packages.

2. Copper sulphate and copper sulphate solutions have been regulated under UN 3010 COPPER BASED PESTICIDES according to Class 6.1 criteria based on the entry "copper compounds" in the List of Common Pesticides. Based on former RID/ADR regulations for Class 6.1 item number 87 (c) solutions with 20 to 100, solid mixtures with 50 to 100 percent copper sulphate had been regulated under Packing Group III of Class 6.1. The comprehensive deletion of the Pesticides Table decided by this Sub-Committee in 1995 removes any citation of copper compounds from the UN Recommendations on the Transport of Dangerous Goods.

3. Oral LD50 values of copper sulphate are 300 and 960 mg/kg rat but e.g. 87 mg/kg mouse. The reason for large species differences is not known mainly because the biochemical mechanism of excessive doses of copper is not well understood.

4. Several cases of accidental or suicidal ingestion have shown that a total of less than 500 mg copper, equivalent to less than 30 mg/kg, have been fatal for children. The fatal dose for adults is difficult to estimate because of vomiting, but it is about 140 mg/kg. The corrosive effect of large doses of copper sulphate to mucous membranes in the gastrointestinal tract leads to shock. Patients often die in shock 2 or 3 hours after ingestion. If they survive, the absorption of copper produces severe hemolysis, icterus or liver granulomas or/and renal failure. Therefore, classification of copper sulphate solutions has to be based on human experience.

5. Solutions of copper sulphate are not corrosive to iron and galvanized iron according to criteria of Class 8, but pitting corrosion has been reported.

6. The strong toxic effect of copper solutions on water organisms and the potential for accumulation of copper mainly in shellfish leads to a classification of copper sulphate according to the scientific criteria of RID/ADR and IMDG Code although not listed by name.

7. Deletion of entries in dangerous goods regulations, toxicological extrapolations based on human experience, suspicion of corrosion on metal surfaces, and data on strong toxicity to aqueous organsims are confusing industry and authorities leading to many inquiries concerning classification.

8. A Data Sheet for Substances Submitted to the United Nations for New or Amended Classification based on copper sulphate solution and data on solid copper sulphate is attached.

Proposal

9. Based on measurements, scientific extrapolations and practicability following amendments to the Recommendation are proposed:

Add to chapter 2:

3xxx	COPPER SULPHATE	6.1	ABC	III
3XXX	COPPER SULPHATE SOLUTION	6.1	XYZ	III

Add special provision:

ABC Based on human experience solid mixtures or preparations containing less than 50 percent copper sulphate are not subject to these Recommendations. Such goods may be subject to regulations for environmentally hazardous substances (e.g. Marine Pollutants).

XYZ Based on human experience solid mixtures or preparations containing less than 25 percent copper sulphate are not subject to these Recommendations. Solutions with less than 25 percent copper sulphate may be subject to regulations for environmentally hazardous substances (e.g. Marine Pollutants).

Add to index:

Copper sulphate pentahydrate, see	6.1	3xxx
Copper sulphate pentahydrate solution, see	6.1	3XXX

*****

Annex

Figure 1.1

DATA SHEET FOR SUBSTANCES SUBMITTED TO THE UNITED NATIONS FOR NEW OR AMENDED CLASSIFICATION

Submitted by GERMANY Date AUGUST 1996

Supply all relevant information including sources of basic classification data.
Data should relate to the product in the form to be transported.
State test methods.
Answer all questions - if necessary state "not known" or "not applicable" - If data is not available in the form requested, provide what is available with details.
Delete inappropriate words.

Section 1. SUBSTANCE IDENTITY

1.1 Chemical name COPPER SULPHATE SOLUTION

1.2 Chemical formula $CuSO_4/CuSO_4 \cdot 5\,H_2O$

1.3 Other names/synonyms BLUE VITRIOL, CUPRIC SULFATE

1.4.1 UN number 3XXX 1.4.2 CAS number 7758-99-8 / 7758-98-7

1.5 Proposed classification for the Recommendations

1.5.1 proper shipping name (13.3 */)

1.5.2 class/division 6.1 subsidiary risk(s)

packing group III

1.5.3 proposed special provisions, if any see proposal

1.5.4 proposed packing method

Section 2. PHYSICAL PROPERTIES (Data for solid pure substance)

2.1 Melting point or range ../.. °C

2.2 Boiling point or range ./.. °C

2.3 Relative density at :

2.3.1 15 °C ... 2.3

2.3.2 20 °C ... 3.6

2.3.3 50 °C ...

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*/ *This and similar references are to chapters and paragraphs in the Recommendations of the United Nations Committee of Experts on the Transport of Dangerous Goods.*

2.4 Vapour pressure at :

2.4.1 50 °C ... kPa (no vapour)

2.4.2 65 °C ... kPa

2.5 Viscosity at 20 °C (1.10 */) (water) . ... m^2/s

2.6 Solubility in water at ~~20 °C~~ 15 °C 20,9 g/100 ml
0 °C 14.3 g/100 ml

2.7 Physical state at 20 °C (1.10 and 1.15 */) ~~solid~~/liquid/~~gas~~

2.8 Appearance at normal carriage temperatures, including colour and odour
odorless,, metallic taste, colourless .....
.....

2.9 Other relevant physical properties . 200 - 650 °C decomp. to cupric oxide .....

Section 3. FLAMMABILITY

3.1 Flammable vapour not relevant (solution in water)

3.1.1 Flash point (5.4 */) ... °C oc/cc
3.1.2 Is combustion sustained? (5.7 */) yes/no

3.2 Autoignition temperature ... °C

3.3 Flammability range (LEL/UEL) ... %

3.4 Is the substance a flammable solid ? yes/no

3.4.1 If yes, give details (also complete 4.5.1 and 4.5.2 if relevant)(1.21 */) .....
.....

Section 4. CHEMICAL PROPERTIES

4.1 Does the substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent hazardous reactivity ? ~~yes~~/no

If yes, state

4.1.1 Inhibitor/stabilizer used .....

4.1.2 Alternative method .....

4.1.3 Time effective at 55 °C .....

4.1.4 Conditions rendering it ineffective .....
.....

**/ This and similar references are to chapters and paragraphs in the Recommendations of the United Nations Committee of Experts on the Transport of Dangerous Goods.*

4.2 Does the substance react with water ? ~~yes~~/no

4.2.1 If yes, state effects . . . . . .

4.3 Does the substance have explosive properties ? (4 *) ~~yes~~/no

4.3.1 If yes, give details . . . . . .

4.4 Does the substance have oxidizing properties ? (1.22 *) ~~yes~~/no

4.4.1 If yes, give details . . . . . .

4.5 Is the substance a self-reactive substance (1.21 *) or an organic peroxide (1.22*)? ~~yes~~/no

If yes, is temperature control required (11.3.5/14.2.2.5 *)? ~~yes~~/no

If yes state

4.5.1 proposed control temperature (11.3.5.3 *) . . . . °C

4.5.2 proposed emergency temperature (11.3.5.3 *) . . . . °C

4.6 Corrosivity (8 *) to :

4.6.1 mild steel pitting corrosion reported mm/year at . . . . °C

4.6.2 aluminium 0,2 . mm/year at . 20 . °C

4.6.3 other packaging materials (specify) . . . . .

5.4 Saturated vapour concentration at 20 °C (6.3.3 [*]) ../.. ml/m³

5.5 Skin exposure (8 [*]) results not corrosive Exposure time ..... hours/minutes
Animal species .....

5.6 Other data Irritating for skin and eyes .....

.....

5.7 Human experience lowest lethal toxicity 5-50 mg/kg range .....

.....

Section 6. SUPPLEMENTARY INFORMATION

6.1 Recommended emergency action

6.1.1 Fire (include suitable and unsuitable extinguishing agents)
see IMO EMS No. 6.1 + 0.2: foam, water, carbon dioxide .....

6.1.2 Spillage hazardous to the aquatic environmental, prevent spreading of substance
absorb in sand

6.2 Is it proposed to transport the substance in :

6.2.1 Intermediate Bulk Containers (16 [*]) ? ~~yes~~/no

6.2.2 Multimodal tanks (12 [*]) ? ~~yes~~/no

If yes, give details in Sections 7 and/or 8.

Section 7. INTERMEDIATE BULK CONTAINERS (IBCs) (only complete if yes in 6.2.1)

7.1 Proposed type(s) .....

Section 8. MULTIMODAL TANK TRANSPORT (only complete if yes in 6.2.2)

8.1 Description of proposed tank (including IMO tank type if known)

.....

.....

8.2 Minimum test pressure .....

8.3 Minimum shell thickness .....

8.4 Details of bottom openings, if any .....

.....

8.5 Pressure relief arrangements .....

8.6 Degree of filling .....

8.7 Unsuitable construction materials .....

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[*] *This and similar references are to chapters and paragraphs in the Recommendations of the United Nations Committee of Experts on the Transport of Dangerous Goods.*